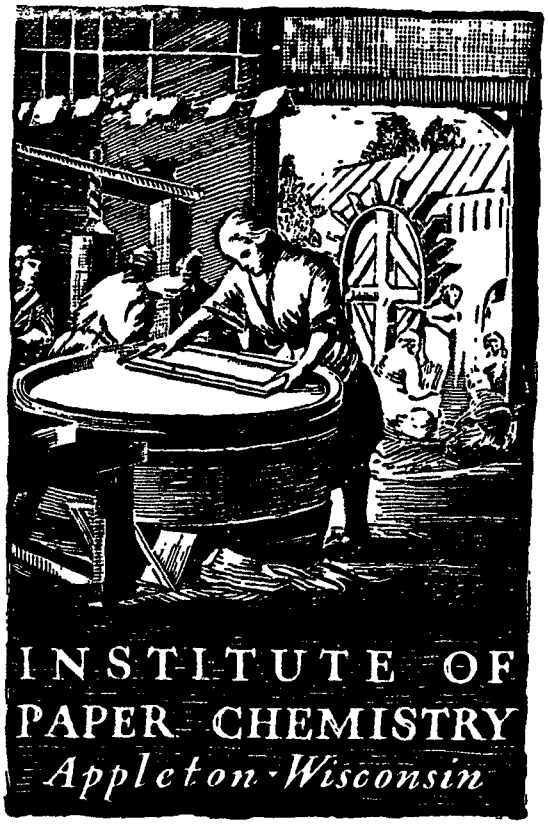

LOSS OF BIPHENYL IN IMPREGNATED CHIPS DURING STORAGE

Project 1108-7-C

Progress Report Two

to

FOURDRINIER KRAFT BOARD INSTITUTE, INC.

September 7, 1954

THE INSTITUTE OF PAPER CHEMISTRY

APPLETON, WISCONSIN

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INTRODUCTION

The introduction of the corrugated paperboard box with ventilation for the packaging and shipment of oranges has necessitated the use of a preservative in order to prevent the decay caused by blue mold and stem rot. The only preservative which has been used successfully to date has been biphenyl. A number of methods have been proposed for adding biphenyl. The current practice used in the Florida citrus industry has been to coat the inside flaps and end panels of the orange box with a hot-melt mixture composed of fifty per cent biphenyl and fifty per cent wax. The citrus packers on the West Coast have inserted impregnated pads in the top of each box. These pads are impregnated with the biphenyl mixture. On the other hand the citrus packers in the Near East have adopted the practice of printing the biphenyl on the inside of the box. It is understood that the die contour is such that the biphenyl is printed in dots similarly to the pattern obtained in half-tone printing except, of course, much larger dots. The biphenyl is applied just slightly above the melting point so that it solidifies immediately on contact with the paperboard.

A few years ago a patent (No. 2,607,694) was granted to A. J. Rinck which utilized small "chips" or pieces of paper or paperboard as

a carrier for the preservative. The suggested practice is to coat or impregnate these chips, which may be of different sizes and shapes, with the preservative and then distribute the thus treated chips in the boxes. Among the advantages of this latter method is that it permits the addition of a definite amount of biphenyl in contrast to the coating of the container which may be used immediately after impregnation or be stored for a number of months. Under the latter conditions the biphenyl may vaporize and thus be partially dissipated by the time the container is used.

The Institute of Paper Chemistry has made a number of experimental runs for the production of these chips in connection with holding trials and trial shipments. One of the points to be considered, should this method of adding the preservative become standard practice, is the type of container to be used for shipment and storage. Preliminary examination of a number of packaging materials indicated that a multi-wall paper sack with a polyethylene liner appeared practical from a performance standpoint. One of the important considerations of a container for this purpose is that it not transmit the biphenyl vapors readily, otherwise the biphenyl would be dissipated, thereby losing one of the salient features of the Rinck method. Therefore, the proper container should be one which not only withstands the hazards of shipment but which acts as a barrier to the passage of biphenyl vapors. This is important not only during the packing season but also between seasons in case chips need to be carried over or stored for the next season.

Although the preliminary tests on the polyethylene-lined paper sacks indicated a desirable performance, it was felt that it would be worthwhile to actually determine the loss of biphenyl-treated "chips" packed and stored under conditions which might be encountered in the "off" season in Florida. Chips were stored under two conditions, one representing normal and the other extremely severe conditions. The biphenyl content was determined periodically throughout the storage period.

MATERIALS USED

The treated chips used in this study were taken from a supply prepared for use in a trial shipment of oranges. The chips were impregnated on two sides with a 50-50 mixture of biphenyl-wax. The degree of impregnation was such as to give approximately 14.5% biphenyl (29.0% biphenyl-wax).

The containers used for test purposes were the same as had been used for shipping the chips from Appleton to Tampa, Florida, and consisted of a 4-ply (50-lb.) multi-wall unbleached kraft paper sack with an inner liner or bag of 2-mil polyethylene. The polyethylene inner sack was closed with a tied closure. The paper sack, which was a sewn bottom open-mouth type, was closed by stapling.

Two conditions of storage were used. One was storage in the loft of the Container Building at The Institute of Paper Chemistry. This area was up under the roof and was exposed to normal atmospheric conditions of temperature and humidity. Being directly under a roof

covered with asphalt paper coated with hot asphalt without adequate ventilation probably subjected the treated containers to a more severe condition of storage than would normally be encountered. The other condition was purposely selected to give the most severe conditions and consisted in storage on the roof of the Container Building. The test bags were placed in the open on the roof. The roof on which the bags were placed consisted of asphalt roofing paper coated with hot asphalt. No covering was provided for the bags; thus, they were exposed to the elements--sun, rain, etc.

At the start of the storage period a sample was withdrawn from each test bag for biphenyl content analysis. Samples were also withdrawn periodically thereafter in order to determine the change in biphenyl content with time. The test periods analyzed to date are given below:

Loft Storage (inside)	Roof Storage (outside)
6-3 (start)	6-3 (start)
7-16	7-16
8-24	8-24
9-10	9-10

The biphenyl content of the chips was determined as follows: The chips were cut into 1/8 to 3/16-inch squares and placed in a 1-liter round-bottomed flask connected to a liquid-liquid extractor. Approximately 300 ml. of water was added to the flask and the contents boiled for 3 hours. Under these conditions the biphenyl is transferred to heptane

(purified) in the liquid-liquid extractor. The biphenyl content is then determined spectrophotometrically with ultraviolet light.

DISCUSSION OF RESULTS

As mentioned previously, this preliminary study was undertaken to determine the extent of the biphenyl loss of biphenyl-treated chips packed in a 4-ply multi-wall sack with a 2-mil polyethylene inner sack under different conditions of storage. The results obtained to date using two conditions of storage are given in Table I and illustrated in Figures 1 and 2.

TABLE I

RESULT OF STORAGE TEST ON TREATED CHIPS

Storage Periods, days	Biphenyl Content, % Loft Storage (indoors)	Roof Storage (outdoors)
0	14.3	14.5
43	13.9	13.2
82	14.0	12.0
103	14.0	12.6

It would appear on the basis of the above results that the biphenyl content of the chips stored indoors in the loft did not change significantly during the first three-month period. On the other hand the chips stored outside on the roof where they were exposed to sun, rain, changing temperatures, etc., show a loss of approximately 2% in biphenyl content during the first three-month

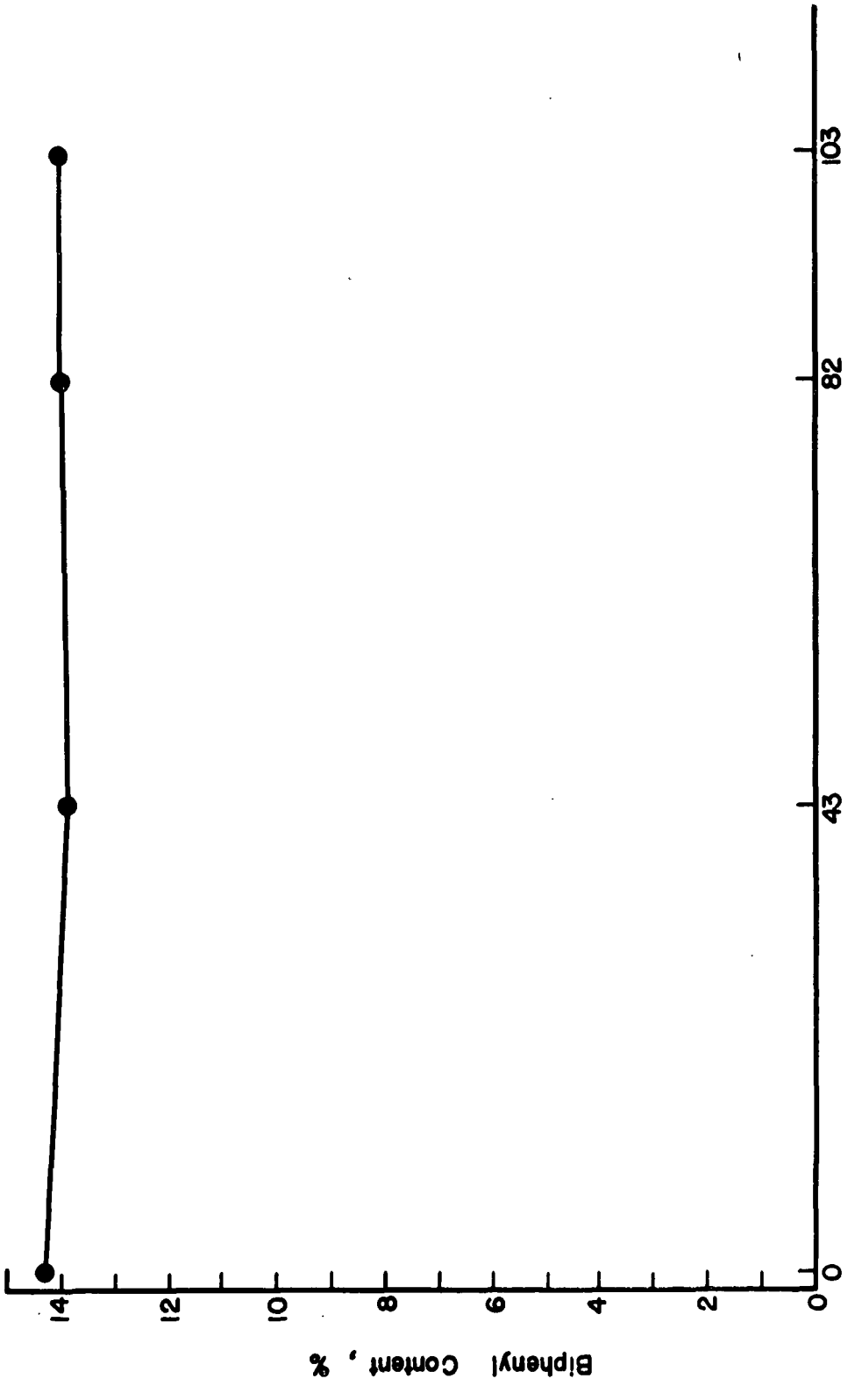

Figure 1. Comparison of Biphenyl Content of Chips Stored Indoors in Loft with Time.

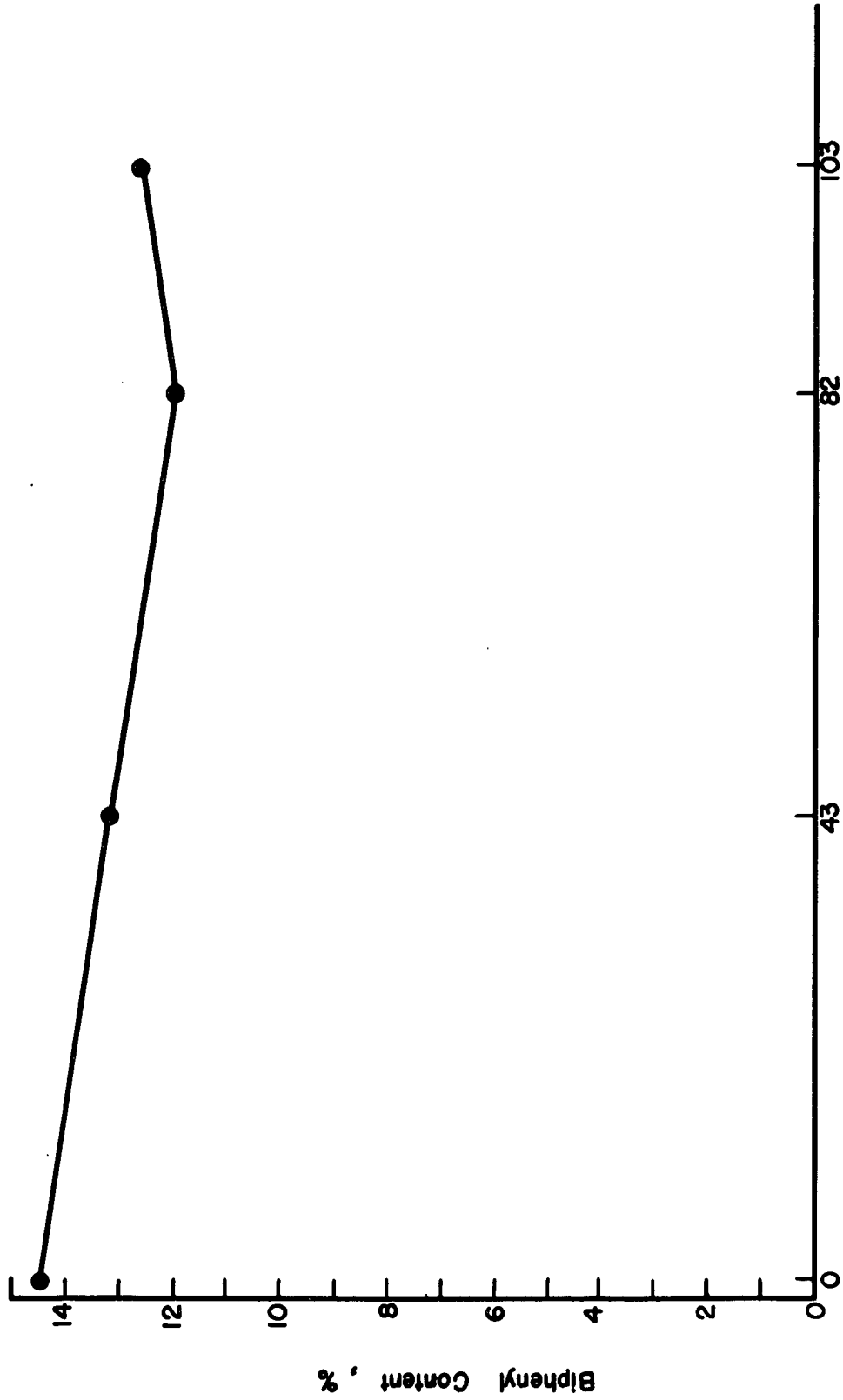

Figure 2. Comparison of Biphenyl Content of Chips Stored Outdoors with Time

storage. It was observed in the case of the roof-stored chips that the upper face of the bags were coated on the inside with biphenyl. Apparently during the extreme heat of the day the temperature rose to such a level that a considerable quantity of biphenyl vaporized and then condensed on the walls of the bag when the temperature dropped. No attempt has been made as yet to determine the amount of biphenyl condensed on the sidewalls of the bag. This will be done when the storage period terminates. The above-mentioned phenomenon was not observed in the case of the baga stored indoors in the loft.

It would appear from the results presented above that the containers used in this study are adequate in so far as a biphenyl barrier is concerned when stored indoors. When stored in such a way that the direct rays of the sun fall on them, a small loss of biphenyl is anticipated. Although the storage period used in this study has extended over only a 103-day period (approximately 3 months), it is to be expected that the same trends as encountered to date will prevail over a longer period. However, the study is being continued for another three-month period.